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Review

HISTORICAL REVIEW ON RESEARCH OF KINETICS IN THERMAL ANALYSIS AND THERMAL ENDURANCE OF ELECTRICAL INSULATING MATERIALS

I. Thermal endurance test and isoconversion methods

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Abstract

In 1925 a paper on kinetic analysis of data obtained with thermobalances for isothermal mass loss of some natural products for electrical insulation was published. This is the first theoretical and experimental approach to accelerated test of electrical insulating materials and also to kinetic analysis of thermal analysis data at isoconversional points. In succeeding papers, change in chemical composition and kinetics under temperature change were dealt with. A historical review of these two topics is described in this review article, especially on the basic concept commonly induced for these two fields.

Keywords: historical review, isoconversion methods, kinetics, thermal endurance test

Introduction

Thermal endurance of insulating materials has direct influence on life of electrical machines, cables and other electrical equipments. The temperature is raised by energy loss during operation, and these materials undergo thermal deterioration during a long service, for example for 10 years. Therefore, it has

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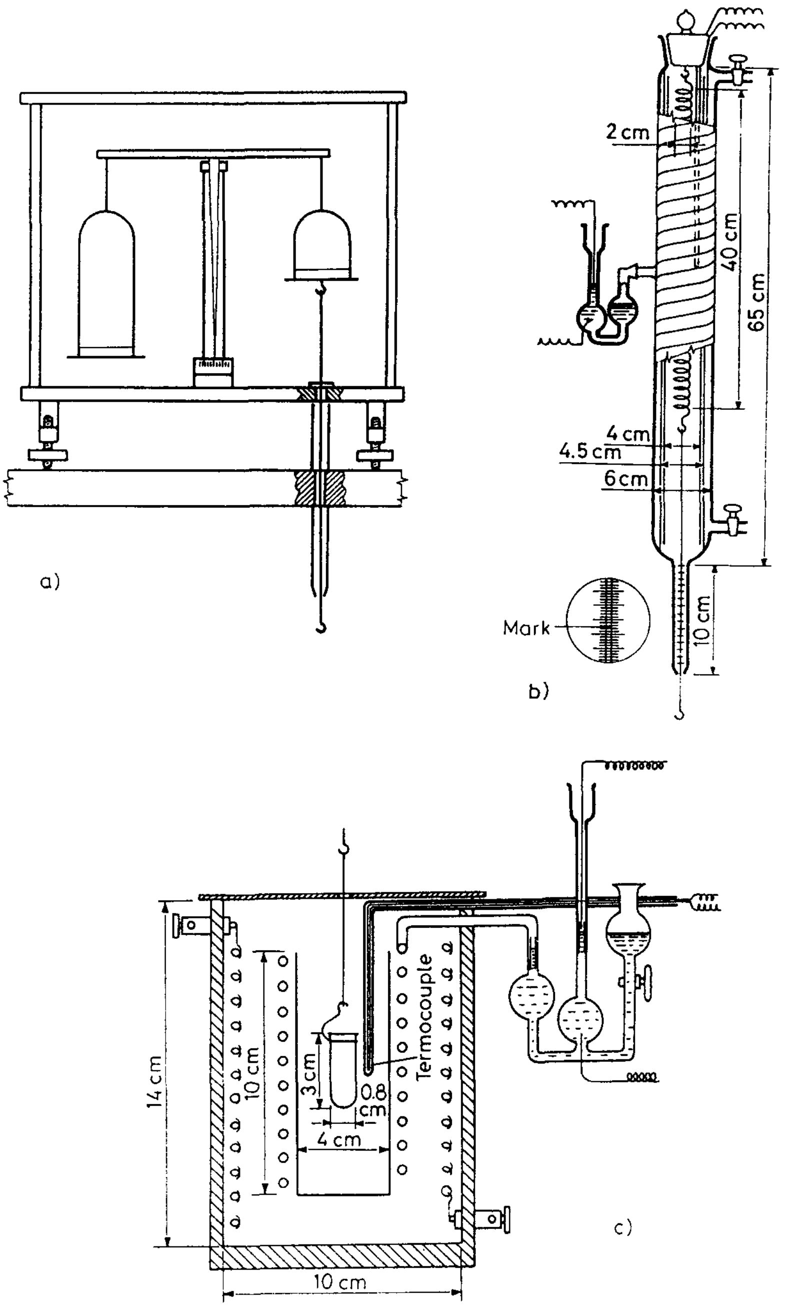

Fig. 1 Thermobalances used by Kujirai and Akahira [1]: (a) a chemical balance, (b) a spring balance and (c) a sample container and a furnace with a temperature controller. All figures in this paper are reproduced figures of the original paper [1]

been an important problem to evaluate thermal endurance of these materials, and it has been investigated hitherto for a long time.

To evaluate their thermal endurance, kinetic analysis of isothermal data with thermobalances was first made and published in 1925 [1]. A method for evaluating thermal endurance of electrical insulating materials was also proposed by using these results [1]. The concept derived in this work is also the same as the base of a few methods for kinetic analysis of thermoanalytical data proposed later [2]. Thus the two topics, i.e., kinetics in thermal analysis and thermal endurance evaluation are connected with each other from the very beginning. However, these two accomplishments had not been succeeded and developed furthermore.

Afterward, thermogravimetry and differential thermal analysis have been used for evaluating thermal endurance of electrical insulating materials, and applicability of thus obtained results to the thermal endurance evaluation has also been discussed for a long time. Evolved gas analysis by stepwise heating and cooling was proposed later for this purpose and it has been investigated to establish a short-time test method for thermal endurance evaluation.

In this paper the above-mentioned progress in a branch of thermal analysis is reviewed from historical viewpoint. Part I is to reveal pioneering works of high priority and also to describe their relation with the methods for kinetic analysis of thermoanalytical data. In part II thermal analysis application to the thermal endurance evaluation of electrical insulating materials will be described, and several attempts to apply thermal analysis for this purpose will be critically reviewed.

First work by Kujirai and Akahira

A paper on the subject was published by Kujirai and Akahira in 1925 [1]. This is among first papers on the subject, especially on theoretical approach, and insulating materials of natural products, such as cotton, paper and silk, were tested with a thermobalance. Two points of excellent originality were described in the paper; one is a fundamental concept on accelerated test method for thermal endurance evaluation, and the other is a kinetic aspect of thermal analysis.

Experimental results

Mass loss of the materials at relatively high temperatures was observed with two types of thermobalance, i.e., a spring balance and a chemical balance, as shown in Fig. 1 [1]. The sensitivity of the balances was very high; less than 0.05 mg mass loss was detected with the chemical balance and 0.1–0.5 mg change could be detected with the spring balance. The temperature of the furnace was precisely controlled with a fluctuation less than 1°C by using a sophisticated regulator and an electrical circuit. The chemical balance was used for low rate mass loss in a low temperature range, while the spring balance was applied to fast mass loss in a high temperature range.

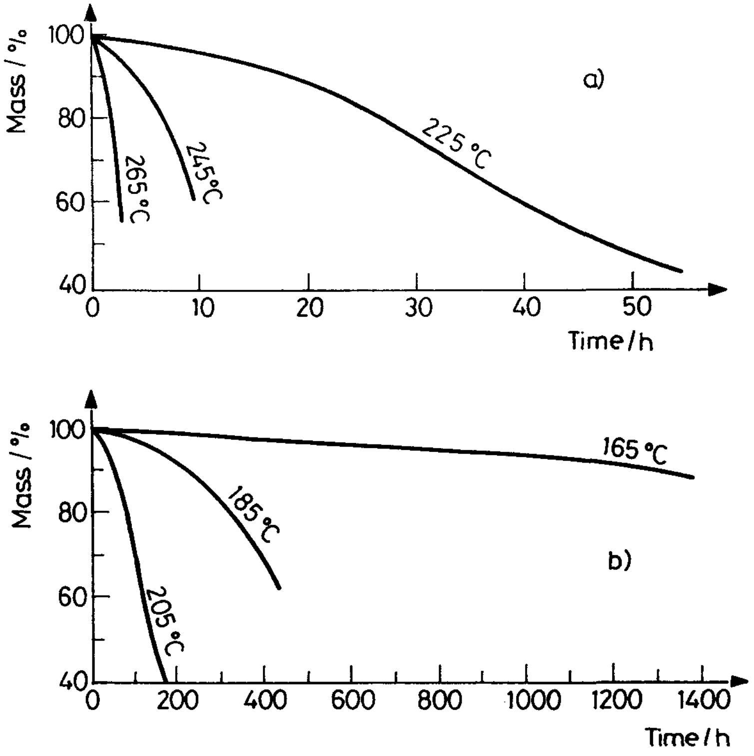

Fig. 2 Mass loss curves of cotton at indicated temperatures [1]: (a) high temperature range and (b) low temperature range. The term "weight" was used in the original paper by Kujirai and Akahira instead of mass

The samples were cotton, filter paper for chemical analysis, linen, manila paper, silk and Empire cloth which is cotton cloth treated with linseed oil.

Examples of the mass loss curves at different constant temperatures are reproduced in Figs 2 and 3 [1]. Similar results were observed for the other samples.

The following relation was found for the mass loss curves:

$$\ln t = \frac{Q}{T} - f(m) \tag{1}$$

where t, T, m and Q are respectively the time, the absolute temperature, the mass (in percent) and a constant, and f(m) means a function of the mass[*]. Q and f(m) were both characteristic of the material. Therefore, a linear plot could be obtained, when the logarithm of the time was plotted against the reciprocal absolute temperature at a given mass loss. The linear plots obtained at different mass losses for the same material were parallel with each other, and hence the constancy of Q value was ascertained, as seen in Fig. 4. Similar results were also obtained for the other samples. When f(m) was plotted against m, smooth curves were obtained for all materials (Fig. 5, as examples).

Because mechanical and electrical properties are principal factors limiting the life, relations of these properties with the mass loss were observed at different ageing temperatures [1].

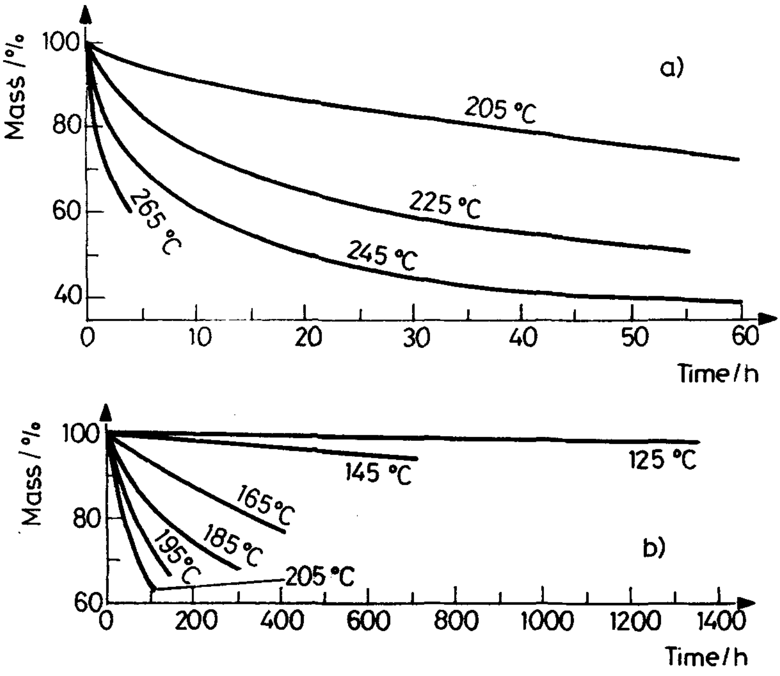

Fig. 3 Mass loss curves of silk at indicated temperatures [1]: (a) high temperature range and (b) low temperature range. The term "weight" was used in the original paper by Kujirai and Akahira instead of mass

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[*] In the original paper [1], the weight, w, in percent was used instead of the mass, m

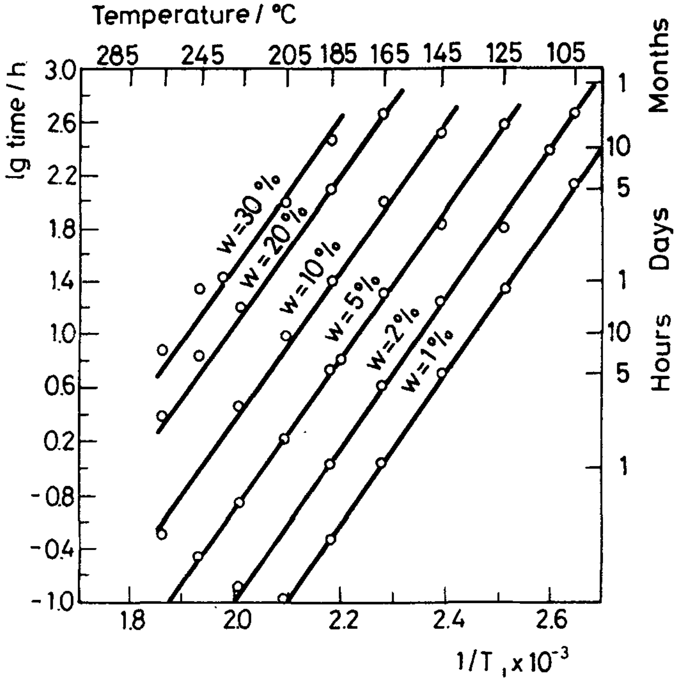

Fig. 4 Plots of logarithm of time *vs.* reciprocal absolute temperature for Empire cloth [1]. The symbol *w* for the weight was in the original paper by Kujirai and Akahira and it is equivalent to *m*

Tensile strength of partially deteriorated samples of manila paper was found to be a single value function of the mass, as seen in Fig. 6, and similarly bending strength was also the case for Empire cloth. Namely,

$$P = g(m) \tag{2}$$

where P denotes the mechanical properties and $g(m)$ is a single value function of m. Therefore,

$$\ln t = \frac{Q}{T} - h(P) \tag{3}$$

where $h(P)$ is also a single value function of P and it is characteristic of the material.

Method for evaluating life

From the above experimental results, a method was proposed to evaluate the isothermal life for the deterioration [1].

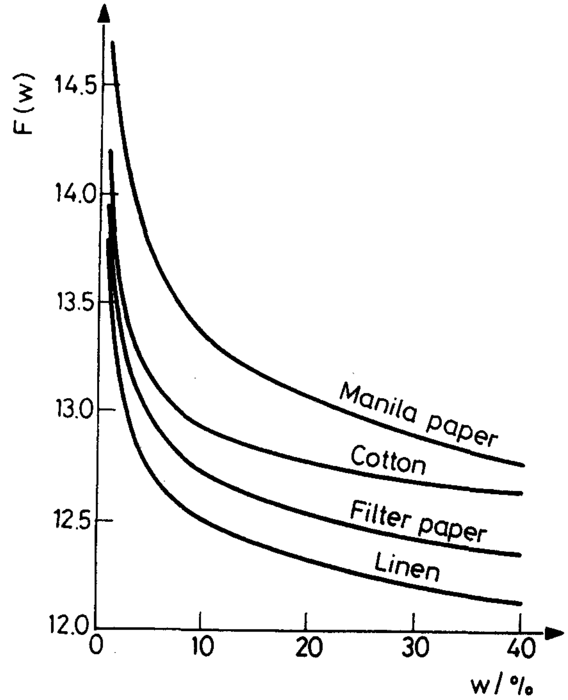

Fig. 5 A curve of f(m) *vs.* m for manila paper, cotton, filter paper and linen [1]. The symbol w for the weight was in the original paper by Kujirai and Akahira and it is equivalent to m. F(w) on the ordinate is equal to f(m)

The material can not be used furthermore beyond the time at which the property deteriorates to a given extent. The mass loss corresponding to the given extent of the deterioration can be obtained using the experimental relation such as Eq. (2). Then, the life time for the corresponding mass loss at the operating temperature can be estimated by extrapolation of the above linear plot or by Eq. (1) using Q and f(m).

This is essentially the same that Dakin proposed afterward in 1948 [3] and that described in the present standard test method [4]. Only the difference is that Dakin and the standard test method used directly the relation expressed in Eq. (3); the deterioration of the properties was observed at relatively high temperatures, and the life at a low operating temperature was estimated by extrapolating the linear plot of the logarithm of the life at the high temperatures *vs.* the reciprocal absolute temperature [see Eq. (3)]. Thus the fundamental concept of the modern standardized accelerated test method [4] had been established by Kujirai and Akahira [1] and by Dakin again but in more straight and clear form [3].

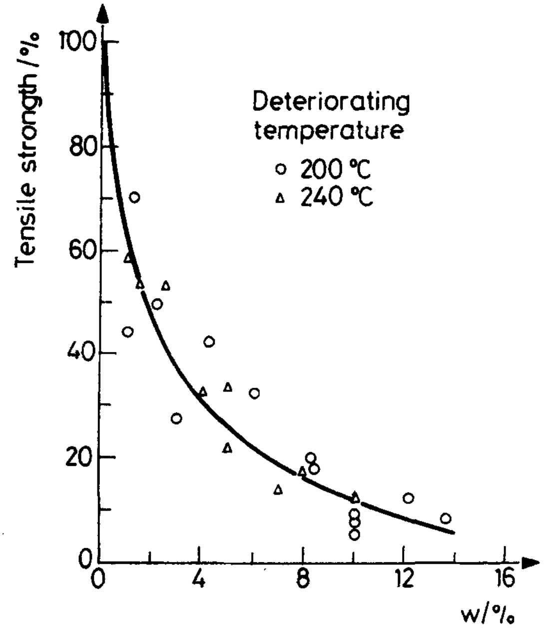

Fig. 6 Relation between tensile strength and mass loss for manila paper [1]. The symbol *w* for the weight was in the original paper by Kujirai and Akahira and it is equal to *m*. Test conditions: Temp.: 21°C; Rel. Humidity 42.5%; Pressure: 766.0 mmHg

Other papers by Akahira

Relation with chemical aspect of process

From Eq. (1) Akahira derived a differential equation;

$$\frac{\mathrm{d}m}{\mathrm{d}t} = C\exp\left(-\frac{Q}{T}\right) f'(m) \tag{4}$$

where C is a constant and $f'(m)$ is another function of m, and he pointed out similarity of this equation to the kinetic equation for chemical reactions [5]. From this consideration, he observed change of the composition of elements in cellulose under deterioration, i.e., carbon, oxygen and hydrogen [5].

The contents of the three elements in the partially deteriorated samples of cotton cellulose were analyzed and their relation with the mass loss was observed. The contents of three elements changed linearly with the mass loss, and the relations were independent upon the temperature conditions, either a constant or varying temperature. It could be induced that the same chemical reaction proceeded in the above deterioration irrespective of the temperature change.

Kinetics under temperature change

Akahira extended the above results to non-isothermal deterioration and derived a concept of "equivalent temperature" for the effect of varying temperature [5].

Mass loss proceeding at a temperature T_1 for a time interval t_1 and then at T_2 for t_2 was compared with that at T_2 for cotton. The latter parts of the both curves were coincident with each other very well, and the mass loss at T_2 for t_2 and then T_1 for t_1 was also the same. This fact suggested that Eq. (4) is applicable not only to isothermal processes but also to those under temperature change. This was also ascertained by the above-mentioned linear relation of the contents of the elements with the mass loss. Thus the following equation was derived for regular cyclic temperature change, and the new concept of the "equivalent temperature ", T_e, was proposed;

$$T_e = Q / \ln \left[\int_0^{P} \frac{\exp\left(\frac{-Q}{T}\right)}{p} \mathrm{d}t \right] \tag{5}$$

where p is the period of the cycle. The deterioration under the cycle proceeds at the same rate as that proceeding isothermally at T_e. Similar mathematical treatments were derived afterward by Frentz for thermal deterioration of electrical insulating materials [6].

Furthermore, Akahira [7] published a numerical table for exponential integral function, which is necessary for calculating the integral in Eq. (5) for heating and cooling at a constant rate and also for exponential heating and cooling. In the paper it was also stated that the table is also useful in similar calculation for chemical reactions, such as thermal decomposition [7]. A similar table was published afterward by Doyle [8].

Thus these papers by Akahira are the first experimental and theoretical papers on non-isothermal kinetics.

Kinetics of thermal analysis

A thermobalance was invented by a Japanese scientist, Honda in 1915 [9], and it was in 1925 that a paper on a study of thermal decomposition with a thermobalance was first published by a scientist in another country. In those period a thermobalance was being used only in Japan. Therefore, the paper by Kujirai and Akahira [1] seems the first paper dealing with kinetic analysis of experimental data obtained with a thermobalance and a pioneering work also from the viewpoint of kinetics in thermal analysis discipline, because the other thermal analysis then used was only differential thermal analysis, which is not suitable for kinetic observation.

The basic concept for the above linear plot by Eq. (3) and for the accelerated deterioration test is that the extents of chemical reaction or mass loss under different temperature conditions are the same with each other when the extents of deterioration of a certain physical property are the same [Eq. (2)]. Although it was not clearly described neither in Akahira's papers [5, 7] nor in the paper by Kujirai and Akahira [1], the time integral in Eq. (5) is the same at the same extent of deterioration, and it is a measure for extent of deterioration and chemical reaction. This is also the very base for isoconversion methods of kinetic analysis of thermoanalytical data [2]; in the isoconversion methods relations at the same conversion are used for kinetic analysis.

From this principle, Akahira and one of the present authors [10] derived afterward in 1969 an equation to estimate the activation energy, which equals to Q divided by the gas constant, R, using an approximation for the exponential integral function [2, 8]. For kinetics of both thermal deterioration and thermal analysis, another of the present authors [11] introduced a new concept, the reduced time, which equals to the time integral in Eq. (5) [11] and is a single function expressing the extent of process, both in chemical reaction and in thermal deterioration [11, 12]. He also derived a simple isoconversion method for estimating the activation energy from thermal analysis data [11]. These isoconversion methods are both most reliable methods for kinetic analysis [2].

It should be noted that Kujirai and Akahira derived a method to estimate temperature dependence Q of the thermal deterioration by using temperatures and times at isoconversional points, and Akahira proposed the new concept, "the equivalent temperature". Combining these two we can derive present isoconversion methods by using approximation, but they did not reached to the methods or the basic concept that the integral is the same at isoconversion of the mass loss or the property change and that it is a single measure of extent of reaction. To get insight into the kinetics, the concept of the equivalent temperature is not so good as the reduced time, because the fundamental measure for the extent of process must have dimension of time but not dimension of temperature.

Concluding remarks

It is clearly shown from the above description that works done by Kujirai and Akahira were really pioneering ones in the research on thermal deterioration of industrial materials such as electrical insulating materials and also in kinetic aspect of thermal analysis. However, they had not reached to the above-mentioned clear principle, and they did not distinctly describe fundamental concepts contained in their works. Moreover need to evaluate thermal life of insulating materials was not so keen in those days as after the second world war when usage of newly developed synthetic polymers began. Similarly, thermal analysis was not as popular as at present, because it needed long tedious labour before the second world war when automation was about to be introduced into scientific experiments, and need for kinetic analysis of thermal analysis data was also not as high as in recent years. These are presumably the reasons for the fact that their works had not been succeeded by any successors.

Appendix

A brief description of Kujirai and Akahira is given below.

Professor Tsunetaro Kujirai was born in Tokyo in 1884. He graduated from Department of Electrical Engineering, Tokyo Imperial University in 1907 and in the next year he became an associate professor in the department after one year service in the Ministry of Posts and Telecommunications. In 1918 he was promoted to be a professor and concurrently became a researcher in the Institute for Physical and Chemical Research, i.e., Rikagaku Kenkyusho (the abbreviated name is RIKEN and it was established in 1917), one of centers of excellence in Japan. He presided a research group as a chief scientist and made research works in RIKEN until 1925. In 1935 he passed away in Tokyo and until then he was engaged in research and education as a professor in the department, while he spent two years since 1912 in Germany, England and U.S. to study electrical engineering and communication. His main research field were electrical engineering and communication, especially wireless telecommunications including optical communication, and he was given the Imperial Academy Award in 1916 for his accomplishments in this field. He had interest in chemistry and also carried out research on electrical insulating materials, especially heat resistant wire, and along this research he invented dense anticorrosive aluminum oxide coating on aluminum by anodic oxidation in oxalate solution and water vapour treatment under high pressure. This is well known as Alumirite in U.S., Alumite in Japan and Bengough in U.K.

Professor Takeo Akahira was born in Aomori in 1895. He graduated from Department of Electrical Engineering, Tokyo Imperial University in 1920. After graduation he became a research assistant in RIKEN under Prof. Kujirai and got a post of chief scientist afterward. He concurrently served as a lecturer in the department from 1925 to 1935, while he stayed in U. S. for one year. His research field spreaded widely from electrical insulating materials, such as enamelled wire, and carbon film resistors to purification of streptomycin with ion exchange resins. It should be noted that he also commercialized these research accomplishments. From 1964 to 1976 he devoted himself to education as a professor in Department of Electrical Engineering, Chiba Institute of Technology. In 1981 he passed away.

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Zusammenfassung — 1925 wurde ein Artikel über kinetische Analyse von Daten veröffentlicht, die mittels Thermowaagen für den isothermischen Massenverlust einiger Naturprodukte für elektrische Isolationen erhalten wurden. Dies ist die erste theoretische und experimentelle Methode zur Beschleunigung von Tests von elektrischen Isolationsmaterialien und auch für die kinetische Analyse thermoanalytischer Daten an Isokonversionspunkten. In folgenden Artikeln wurden Änderungen der chemischen Zusammensetzung und die Kinetik bei Temperaturänderungen behandelt. Vorliegend wird ein historischer Überblick über beide Themen gegeben, insbesondere auf der Grundlage des für diese beiden Gebiete häufig herbeigeleiteten Grundkonzeptes.